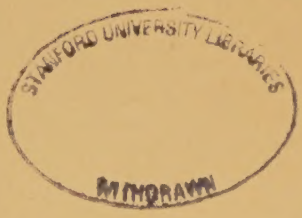
A NEW METHOD FOR THE GRAVIMETRIC DETERMINATION OF URANIUM.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science,
Columbia University.

BY

ANDREW C. RICE



NEW YORK CITY
1928

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A NEW METHOD FOR THE GRAVIMETRIC DETERMINATION OF URANIUM.

The work presented here uses a new reagent for the quantitative determination of uranium. Present gravimetric methods for uranium involve tedious separations of certain ions which are likely to be present. For instance, some of the most common methods depend upon the precipitation of uranium by ammonium hydroxide or by the phosphate ion. These reagents, however, likewise precipitate so many of the commonly occurring ions as to necessitate preliminary separations involving a number of operations. The methods thus become far from desirable direct methods. A direct separation of uranium from the interfering ions will also improve the volumetric methods, because, in these, the same preliminary separations are required.

In gravimetric analysis the most common method for the determination of uranium is precipitation as uranyl phosphate, which was first suggested by LeConte.[1] The precipitate thus formed is non-crystalline and voluminous, making it difficult to wash free of impurity, and, furthermore, it shows a decided tendency to run through the filter paper.

A review of the literature shows many attempts to improve the physical characteristics of the precipitate and to increase the accuracy of the separation of uranium from ions with which it is associated. Under the former heading, mention may be made of Kern,[2] who suggested the use of ammonium dihydrogen phosphate and Brearley,[3] who advised microcosmic salt. Noyes[4] later recommended using sodium phosphate in the presence of ammonium salts. Kern,[2] however, had used this method previously. Pierle[5] found none of these methods satisfactory. Under the latter heading the more important contributors are the following: Peligot[6] recommended the precipitation of diammonium uranate by ammonium hydroxide. This method was also used by Kern,[2] who stated that after three precipitations the alkaline earths and alkalies were sep-

arated successfully from uranium. This method is also recommended by the Bureau of Mines.[7] In this case, however, it is followed by precipitation as a phosphate. It is quite evident that such common elements as aluminium, iron, manganese, lead, and, in some cases, the alkaline earths seriously interfere with these methods. Kern[2] and Brearley[3] suggested the use of sodium carbonate as a method for separating aluminium and iron from uranium, which remained in solution as double carbonate. The gelatinous character of these precipitates make filtration and washing difficult, and, furthermore, a considerable amount of uranium is carried down by adsorption.

While working with the insoluble arsenate of zirconium, it was noticed that the arsenate of uranium was markedly more insoluble than the arsenates of most other metals. Qualitative experiments showed that the uranyl ion was precipitated as a crystalline arsenate from a hot solution containing acetic acid and ammonium salts. The filtrate from this precipitate gave no precipitate with ammonium hydroxide or potassium ferrocyanide. The formation of this precipitate in an acetic acid solution at once suggested the possibility of separating uranium from all of those ions whose arsenates do not form in acetic acid solution. Furthermore, the crystalline character of this precipitate would at once overcome many difficulties inherent in the methods previously described, all of which involve gelatinous or non-crystalline precipitates.

EXPERIMENTAL PROCEDURE.

Kalbaum's uranyl nitrate was used to make up a solution, 25 cc. of which was approximately equivalent to one-tenth of a gram of uranium oxide U_3O_8. The solution was tested for the more common elements such as iron, aluminum, and the alkaline earths. It was found to be free of these impurities.

Standardization by the Phosphate Ion.

The two most promising procedures for the phosphates were selected from those advocated by the various investigators. The first method tried was the one suggested by Kern.[2] It involves the precipitation of uranyl ammonium phosphate by ammonium dihydrogen phosphate. After thorough diges-

tion the precipitate is supposed to become crystalline in character. An outline of the conditions given by Kern is as follows:

25 cc. of uranyl nitrate solution.
3 cc. of 1—1 acetic acid.
Diluted to 150 cc. with distilled water.
30 cc. of ammonium dihydrogen phosphate (75 grams in one liter).
Brought to a boil and digested for half of an hour.
Filtered, washed with dilute ammonium nitrate water, dried and ignited slowly over a bunsen burner and, finally, over a blast lamp.
Added 2-3 cc. of concentrated nitric acid, and ignited slowly over a bunsen burner.
Weighed as $(UO_2)_2P_2O_7$.

Difficulty was experienced in obtaining the crystalline precipitate. The precipitate also ran through the filter paper. Next, the procedure suggested by Noyes[4] was tried. This procedure had really been used by Kern[2] earlier. This method undertakes to promote the formation of uranyl ammonium phosphate by precipitating with sodium phosphate in ammonium salt solution. The precipitate formed is non-crystalline and yet dense. It appeared to filter a little better than the precipitate obtained in the first procedure, and was used in all of the later work in this paper. An outline of the conditions as given by Kern is as follows:

25 cc. of uranyl nitrate solution.
25 cc. of ammonium chloride (75 grams in one liter).
Diluted to 150 cc.
30 cc. of sodium hydrogen phosphate (75 grams in one liter).
Brought to a boil and digested for five minutes.
Filtered, washed with ammonium chloride water, and dried.
Ignited slowly over a bunsen burner and, finally, over a blast lamp.
Added 2-3 cc. of concentrated nitric acid, and ignited slowly over a bunsen burner.
Weighed as $(UO_2)_2P_2O_7$.

STANDARDIZATION BY AMMONIUM HYDROXIDE.

While the precipitation of diammonium uranate by means of ammonium hydroxide is not to be recommended as a method for the determination of uranium in the presence of other ions,

it was thought that this method might serve for the standardization of pure uranyl nitrate solution. An outline of the conditions is as follows:

25 cc. of uranyl nitrate solution.
150 cc. of distilled water.
25 cc. of ammonium chloride (75 grams in one liter).
25 cc. of 1—1 filtered ammonium hydroxide.
Boiled and digested for five minutes.
Filtered and washed with ammonium chloride water.
Ignited slowly over a bunsen burner and, finally, over a blast lamp.
Weighed as U_3O_8.

It was found that reproducible results were difficult to obtain. If the solution is allowed to stand a few days, the precipitate will disappear entirely. Fairly good results were obtained if the solution was filtered immediately. In the data the manifestly inaccurate results by this method were omitted. Similar difficulties were encountered as noted in the literature.[8, 9, 10, 11]

ARSENATE PRECIPITATION.

It was found necessary to establish the fact that arsenic acid precipitated the uranyl compound quantitatively in acetic acid-ammonium salt solution. After establishing this fact, the effect of varying acetic acid concentration was determined. Finally the effect of mineral acid upon the precipitation was noticed. After experimentation, the following procedure was found to be the best. This procedure was used throughout all of the preliminary work given in this paper. Outline of the procedure is given below:

25 cc. of standard uranyl nitrate solution.
Glacial acetic acid varied as shown in the Table.
Diluted to 200 cc. with distilled water.
25 cc. of ammonium chloride (75 grams in a liter).
35 cc. of arsenic acid (80 grams in a liter).
The solution was brought to a boil, allowed to cool and settle, and filtered.
The precipitate was washed thoroughly with 200-300 cc. of dilute ammonium chloride water, and dried.
Ignited to constant weight (See procedure for ignition, which is included later under the caption, "Notes on the Arsenate Method").

TABLE I.

Ammonium Hydroxide Standardization Weighed as U_3O_8	Phosphate Standardization Weighed as $(UO_2)_2P_2O_7$
0.0697 grams	0.0881 grams
0.0699	0.0877
0.0701	0.0880
0.0698	0.0879
0.0701	0.0880
0.0702	0.0881
0.0700	
0.0697	
Aver. 0.06994 grams	Aver. 0.08797 grams
a.d. 0.00016	a.d. 0.00011
*Calc. U. 0.05932	*Calc. U. 0.05946

Arsenate Determination Weighed as U_3O_8	Percent of Glacial Acetic Acid by Volume
0.0701 grams	10
0.0697	10
0.0700	10
0.0697	15
0.0699	15
0.0702	15
0.0700	20
0.0701	20
0.0701	25
0.0701	25
0.0698	25
0.0699	25
0.0701	25
0.0700	45
0.0701	45
Aver. 0.06998 grams	
a.d. 0.00012	
*Calc. U. 0.05936	

* The uranium calculated was obtained by assuming the formulas generally accepted for the ignited precipitates, and calculating the uranium present. The International Atomic Weight Table for 1925 was used in calculating these factors. The factors were uranium in U_3O_8 — 0.84809 and uranium in $(UO_2)_2P_2O_7$ — 0.67624. See Lundell and Knowles[9] for a recent evaluation of these formulas.

For another uranyl nitrate solution the preliminary results are tabulated below. The concentration of glacial acetic acid was twenty percent by volume.

Ammonium Hydroxide Standardization Weighed as U_3O_8	Phosphate Standardization Weighed as $(UO_2)_2P_2O_7$	Arsenate Determination Weighed as U_3O_8
0.0848 grams	0.1057 grams	0.0849 grams
0.0845	0.1061	0.0847
0.0843	0.1060	0.0845
0.0844	0.1061	0.0847
		0.0845
Aver. 0.08450 grams	Aver. 0.10598 grams	0.0846
Calc. U. 0.07166	Calc. U. 0.07168	0.0844
		Aver. 0.08463 grams
		Calc. U. 0.07177

The effect of small concentrations of hydrochloric acid was next determined. It was found that if the acid concentration exceeded 0.10% by volume, the precipitation by arsenic acid was not quantitative. The precipitation of the uranyl arsenate was found to be incomplete even when large excess of arsenic acid was added.

IRON SEPARATION.

One of the most perplexing problems that presents itself in the gravimetric determination of uranium is its separation from iron. This is usually attempted by precipitation of ferric hydroxide by means of sodium carbonate. Arsenic acid in acetic acid-ammonium salt solution does not precipitate ferric iron when present in small quantities. For larger amounts it seemed possible that reduction of ferric iron to ferrous iron by means of sulfur dioxide might suffice. To test the feasibility of this procedure, the arsenate precipitation was tried in the presence of sulfur dioxide and then in the presence of ferrous iron. The conditions of experiment were similar to those used in the preliminary procedure given above. The solution contained ten percent by volume of glacial acetic acid.

TABLE II.

(25 cc. of saturated sulfur dioxide water) Weighed as U_3O_8	(0.0549 grams of iron as ferrous salt) Weighed as U_3O_8
0.0698 grams	0.0841 grams
0.0699	0.0845
0.0698	0.0844
Standard 0.06998 grams	Standard 0.08450 grams

This shows that neither sulfur dioxide nor ferrous iron interfere with the arsenate precipitation method for the determination of uranium.

Next, the arsenic acid precipitation was tried from a solution in which the ferric iron had been reduced by sulfur dioxide. The results were a trifle low. As more iron was added the larger became this error. This seemed to indicate that the increase in acidity, due to the reduction reaction, probably exceeded the point at which the complete precipitation of the arsenate was possible. To decrease the acidity, experiments were tried, using sodium sulfate and ammonium acetate as buffers. In the use of the latter reagent, a large excess must be avoided, as it tends to produce a non-crystalline precipitate.

Six grams of sodium sulfate, added to each solution before precipitation by arsenic acid, gave the following results. There were 0.0586 grams of iron as ferric sulfate present. Single precipitation was used.

TABLE III.

Grams of U_3O_8 Weighed	Grams of U_3O_8 Weighed
0.0848 grams	0.0846 grams
0.0846	0.0844
0.0843	0.0846
0.0846	0.0845
Average weight of U_3O_8	0.08455 grams
Calculated uranium	0.07171
* Standard uranium	0.07167

* The standard uranium is the average of the calculated uranium for the first forty samples run on that uranyl solution.

These results show that a large quantity of sodium sulfate will buffer the above solution sufficiently to allow a quantitative arsenate precipitation. They also show that this method will give good results in the presence of a large amount of a sodium salt.

After experimentation it was found that ammonium acetate could be used as a buffer under the following conditions. The ammonium acetate solution was made up to contain 20 grams of ammonium acetate to 150 cc. of solution. Five cubic centimeters of this solution were present in 250 cc. of precipitating solution. This concentration was found to be large enough to insure the quantitative precipitation of the arsenate for the concentrations of iron that were used. Iron was present as ferric chloride.

TABLE IV.

Weight of U_3O_8	Iron present	Weight of U_3O_8	Iron present
0.0845 grams	0.0113 grams	0.0844 grams	0.0595 grams
0.0845	0.0113	0.0845	0.0595
0.0849	0.0113	0.0843	0.0595
0.0847	0.0595	0.0845	0.0595
0.0844	0.0595	0.0844	0.0595
0.0845	0.0595	0.0842	0.0595
0.0845	0.0595	0.0843	0.0595
0.0847	0.0595	0.0847	0.0595
		0.0843	0.0595

Average weight of U_3O_8	0.08450 grams
Calculated uranium	0.07172
Standard uranium	0.07167

These results establish the fact that it is possible to separate the uranyl ion from ferric iron by reducing the iron with sulfur dioxide and buffering the acetic acid solution with ammonium acetate. The above results are for single preciptation, but, due to the fact that it is often necessary to use reprecipitation, a *double* precipitation method was developed. This method was first used for the separation of iron and later for the separation of other metallic ions from the uranyl ion. An outline of the conditions used during the last part of this experimental work is as follows:

25 cc. of standard uranyl nitrate solution.
25 cc. of glacial acetic acid.
25 cc. of solution containing the metallic ion separated.
25 cc. of ammonium chloride (75 grams in one liter).
75 cc. of distilled water.
If the metal required reducing; 25 cc. of sulfur dioxide water.
35 cc. of arsenic acid (80 grams in one liter).
5 cc. of ammonium acetate (20 grams in 150 cc.).
Boiled, and allowed to stand.
Filtered, and washed with 200-300 cc. of ammonium chloride water.
Returned the filter paper, with the precipitate, to the original beaker.
25 cc. of glacial acetic acid.
100 cc. of distilled water.
25 cc. of ammonium chloride (75 grams in one liter).
1.7 cc. of ammonium acetate (20 grams in 150 cc.).
Boiled, and allowed to stand.
Filtered, and washed with 200 cc. of ammonium chloride water.
Ignited to constant weight (See directions under the caption, "Notes on the Arsenate Method," given later in paper).

When the glacial acetic acid is added to the precipitate, which was returned to the original beaker, the precipitate does not dissolve. If it is desired to dissolve the precipitate, add 3 or 4 cc. of concentrated hydrochloric acid to the 25 cc. of glacial acetic acid and boil gently. If the hydrochloric acid is present, 5 cc. of ammonium acetate, rather than the 1.7 cc. enumerated, should be used. There were 0.0595 grams of iron as ferric chloride present in the experiment. Below are given the results, using the above double precipitation procedure.

TABLE V.

Weight of U_3O_8	Acids present	Weight of U_3O_8	Acids present
0.0846 grams	Glacial acetic	0.0844 grams	glacial acetic
0.0845	acid with hy-	0.0843	" "
0.0843	drochloric acid	0.0845	" "
		0.0842	" "
		0.0846	" "
	Average weight of U_3O_8	0.08443 grams	
	Calculated uranium	0.07161	
	Standard uranium	0.07167	

Having developed a procedure which gave a satisfactory method for determining uranium and separating it from iron, experiments were made to ascertain its value as a separation from cerium, aluminium, alkaline earths, and magnesium.

SEPARATION FROM CERIUM.

The procedure is identical with the double precipitation method developed with iron, except that cerium nitrate was used instead of ferric chloride. There were 0.1508 grams of cerium as ceric nitrate present. The results from this experimental procedure are given below.

TABLE VI.

Weight of U_3O_8		Weight of U_3O_8
0.0845 grams		0.0845 grams
0.0845		0.0848
0.0845		0.0845
	Average weight of U_3O_8	0.08455 grams
	Calculated uranium	0.07171
	Standard uranium	0.07167

SEPARATION FROM ALKALINE EARTHS.

A group of metals that is universally associated with uranium is the alkaline earth group. Qualitative examination showed that the arsenates of the alkaline earths were soluble in acetic acid solution. This would indicate that it might be possible to precipitate the uranyl ion by arsenic acid in acetic acid-ammonium salt solution, without precipitating the alkaline earths. To test this assumption quantitatively, the double precipitation method given above was used. The sulfur dioxide was omitted.

TABLE VII.

Weight of U_3O_8	Amount of Ca present	Amount of Sr present	Amount of Ba present
0.0842 grams	0.0170 grams	0.0118 grams	....
0.0842	0.0170	0.0118	....
0.0844	0.0170	0.0118	....
0.0844	0.0425	0.0236	0.0095 grams
0.0844	0.0425	0.0236	0.0095
0.0847	0.0425	0.0236	0.0095
0.0846	0.0425	....	0.0190
0.0845	0.0425	....	0.0190
0.0846	0.0425	....	0.0190

Average weight of U_3O_8	0.08446
Calculated uranium	0.07163
Standard uranium	0.07167

These results indicate that it is possible to determine uranium, in the presence of the alkaline earths, by the arsenate method.

SEPARATION FROM ALUMINIUM AND MAGNESIUM.

Other metals that are generally associated with uranium are aluminium and magnesium. Qualitative experiments indicated that neither aluminium nor magnesium are precipitated by arsenic acid under the conditions of the experiment.

TABLE VIII.

Weight of U_3O_8	Amount of Al present	Amount of Mg present
0.0848 grams	0.0151 grams	....
0.0846	0.0151	....
0.0844	0.0151	....
0.0844	0.0375	0.0173 grams
0.0847	0.0375	0.0173
0.0846	0.0375	0.0173
0.0846	0.0375	0.0173

Average of weighed U_3O_8	0.08458 grams
Calculated uranium	0.07174
Standard uranium	0.07167

NOTES ON THE ARSENATE METHOD

Precipitation

After the precipitate was obtained, the solution was generally allowed to stand overnight, to obtain larger crystals. However, in a few cases, the solution was cooled quickly and filtered immediately with good results. The precipitate filters very rapidly, and may be washed thoroughly with ease.

The control of ammonium acetate concentration, within certain limits, is necessary. With a large excess of ammonium acetate, the precipitate separates out in a gelatinous form. With practice the following rule may be used. The ammonium acetate may be added, until the precipitate is just ready to appear, in a cold solution. A crystalline precipitate will come down upon boiling. The quantities of ammonium acetate recommended can be halved or doubled without harmful results.

Ignition

The method used for ignition shortens the time when compared with the procedure for driving arsenic off over a blast lamp. The precipitate and filter paper are ignited slowly over a bunsen burner: (A Rose crucible is recommended). Leaving the crucible over the bunsen, a slow current of hydrogen is passed over the precipitate for a few seconds. The arsenic disappears almost instantaneously. After weighing, the precipitate is ignited in the same manner a second time. In most cases the precipitate is found to attain constant weight with the second ignition. The uranium oxide, U_3O_8, appears to be stable under the above conditions. Continued heating over the blast lamp, with a rapid current of hydrogen, caused a change in the appearance of the precipitate and, may indicate partial reduction.

Limitations of the Arsenate Method

Zirconium arsenate is so insoluble that it will precipitate under the experimental conditions that were used. Luckily zirconium is not often associated with uranyl compounds.

Lead arsenate will also precipitate under the experimental conditions used. Lead will, therefore, have to be removed before the uranyl compound is precipitated by arsenic acid. Lead is universally found with uranyl compounds. It may be removed by precipitation as lead sulfide in acid solution. This process will also remove the other ions whose sulfides are insoluble in acids, such as copper, etc.

Reagent

Arsenic acid was prepared by the method advocated by Youden[12]. Chemically pure arsenious acid was sublimed, and then oxidized by concentrated nitric acid. The excess of nitric acid was removed by adding a few drops of concentrated sulfuric acid, and heating until the acid was driven off. This leaves an arsenic acid free from non-volatile impurities. The arsenic acid solution contained eighty grams of arsenic acid in one liter of solution.

DISCUSSION OF RESULTS

From the results, on the first uranyl solution that was standardized, the average deviations were calculated.

a.d. for ammonium hydroxide method	0.00016 grams
a.d. for the phosphate method	0.00011
a.d. for the arsenic acid method	0.00012

From Table I, and the other tables in this paper, the following results were obtained:

	First solution of uranyl nitrate. Uranium calculated	Second solution of uranyl nitrate. Uranium calculated
Ammonium hydroxide	0.05932 grams	0.07166 grams
Phosphate method	0.05946	0.07168
Arsenate method	0.05936	0.07167

The figure of calculated uranium for the second solution of uranyl nitrate is the average of the first forty determinations using that solution. This is the standard uranium content mentioned a few times before.

		Weight of U_3O_8
Average of first forty determinations		0.08450 grams
Table III	$Fe_2(SO_4)_3$ and Na_2SO_4 present	0.08455 "
Table IV	$FeCl_3$ and ammonium acetate	0.08450 "
Table V	Iron and double precipitation	0.08443 "
Table VI	Cerium separation	0.08455 "
Table VII	Alkaline earth separation	0.08446 "
Table VIII	Al and Mg separation	0.08458 "

These results show that the uranyl ion can be quantitatively precipitated from acetic acid solution containing ammonium salts, using arsenic acid as a reagent. There is nothing which indicates that the precipitate adsorbs other ions from solution in appreciable quantities.

SUMMARY

1. The result of this work furnishes a new method for the determination of uranium.

2. This new method for uranium is more precise than those heretofore proposed.

3. Unlike all preceding methods, the uranium is precipitated as a crystalline compound, which is easy to wash and filter.

4. The precipitate shows remarkably slight tendency to adsorb other ions from solution.

5. The reagents are inexpensive and easy to obtain in the pure state.

6. The precipitate is readily ignited to constant weight, and yields an oxide for which a number of volumetric methods of determination are available.

7. The method offers many possibilities for the successful separation of uranium from its associated elements.

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VITA.

Andrew C. Rice was born in Springfield, Massachusetts, March 13, 1900. He received the degree of B.S. from the University of New Hampshire in June 1923. During the years 1923-1925, he held an appointment as Assistant in Chemistry at that institution. He received the degree of M.S. from the same institution in 1925. He was co-author with H. C. Fogg and C. James on "The Determination of Zirconium and Thorium by Means of Phenylarsonic Acid," published in the Journal of the American Chemical Society, Volume 48, page 893. Since 1925 he has been a graduate student in the Faculty of Pure Science, Columbia University. He has also been a part-time Assistant for the years 1925-1928, and is at present an Assistant, in Columbia College.

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